

Pesticide paddy field model (PADDY) for predicting pesticide concentrations in water and soil in paddy fields

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Abstract: To evaluate the fate of pesticides in paddy fields, the pesticide paddy field model (PADDY) has been developed for predicting pesticide concentrations in paddy fields and the run-off amount of pesticides to the aquatic environment. This model focused particularly on granule formulation because these formulations have been used widely as herbicides on paddy fields in Japan. The behavior of pesticides in paddy fields was assessed by considering the main processes on the basis of a compartment system and the mass-balance equations of pesticides in the compartments were derived from kinetic data. The mathematical model, PADDY, was constructed by numerical solution techniques. A method for measuring the pesticide parameters for this model was also developed. To validate the model, a field experiment was carried out on a paddy field and the concentration changes of pesticides in water and soil were measured. These were in reasonably good agreement with those predicted by PADDY.

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Keywords: mathematical model; environmental fate; pesticide; paddy field; granule formulation

1 INTRODUCTION

Recently, concern has arisen that run-off of pesticides applied to agricultural land and grassland such as golf courses may cause contamination to drinking water sources and have adverse effects on aquatic ecosystems. Japanese regulatory agencies have established water quality regulations and standards for pesticides. Monitoring of pesticides residues has been carried out in public water areas such as rivers and lakes. However, monitoring is costly and time-consuming, and its results represent only one specific location under one set of environmental conditions. Therefore, it is difficult to define the key processes of pesticide fate in a wide variety of environments by monitoring results alone. The mathematical model is a useful tool to supplement monitoring data and to evaluate the environmental fate of pesticides under various conditions.

Pesticides are used under various conditions (i.e. application sites, methods, timing, and formulation types). Therefore, these conditions must be considered in estimating the environmental fate of pesticides. Some simulation models are used routinely in Europe and the United States for the environmental exposure assessment of pesticides. However, only a few models¹ for evaluating pesticide behavior in paddy fields have been developed because the major

agricultural land in these countries are upland fields. In Japan, however, more than half of agricultural lands are paddy fields, where applied pesticides can easily flow out through paddy field water to public water areas.

In this paper, we discuss the Pesticide Paddy Field Model (PADDY) for predicting concentrations of water and soil in paddy fields and the run-off amount of pesticides to the aquatic environment. This model has been focused particularly on granule formulations, since these are used widely as herbicides on paddy fields in Japan. A measurement method for the pesticide parameters used in PADDY was also developed. To validate this model, the predicted concentrations of this model were compared with field experimental data.

2 THEORY AND METHODS

2.1 Notation

A	Area of paddy field (m^2)
C_{in}	Pesticide concentration in inflow (mg litre^{-1})
C_s	Pesticide concentration in soil solid (mg kg^{-1})
C_{s0}	Pesticide concentration in surface soil solids (mg kg^{-1})

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C_{si}	Pesticide concentration in soil solids in the i th sub-surface layer (mg kg^{-1})
C_w	Pesticides concentration in water (mg litre^{-1})
C_{w0}	Pesticide concentration in paddy field water (mg litre^{-1})
C_{wi}	Pesticide concentration in pore water in the i th sub-surface layer (mg litre^{-1})
C_{ws}	Water-solubility of pesticide (mg litre^{-1})
D	Diffusion coefficient of pesticide ($\text{m}^2 \text{ day}^{-1}$)
$DT_{50\text{soil}}$	Half-life of pesticide in soil (day)
$DT_{50\text{water}}$	Half-life of pesticide in water (day)
H	Dimensionless form of Henry's constant
h	Thickness of the diffusion layer (m)
i	Subscript denoting the i th sub-surface layer ($i = 1, \dots$)
K_d	Adsorption coefficient (litre kg^{-1})
K_f	Freundlich adsorption coefficient (litre kg^{-1})
K_L	Overall mass transfer coefficient for the liquid phase (i.e., volatilization rate) (m day^{-1})
K_{oc}	Adsorption coefficient related to organic carbon
k_{des}	Desorption rate constant (day^{-1})
k_{ds}	First-order degradation rate constant in soil (day^{-1})
k_{dw}	First-order degradation rate constant in water (day^{-1})
k_g	Gas film mass transfer coefficient (m day^{-1})
k_l	Liquid film mass transfer coefficient (m day^{-1})
k_s	DS/Vh = dissolution rate constant (day^{-1})
M_0	Weight of surface soil solid (kg)
M_i	Weight of soil solid in the i th sub-surface layer (kg)
MW	Relative molecular mass of pesticide
$1/n$	Freundlich exponent
oc	Organic carbon content in soil (%)
Q_g	Penetration rate of water ($\text{m}^3 \text{ day}^{-1}$)
Q_{in}	Inflow rate of water ($\text{m}^3 \text{ day}^{-1}$)
Q_s	Outflow rate of water ($\text{m}^3 \text{ day}^{-1}$)
S	Surface area of dissolving solid (m^2)
T	Temperature (K)
t	Time (day)
V	Volume of water (m^3)
V_0	Volume of paddy-field water (m^3)
V_i	Volume of pore water in the i th sub-surface layer (m^3)
VP	Vapour pressure of pesticide (mm Hg)
W	Amount of pesticide in the granule formulation (mg)

2.2 Model concept

Figure 1 shows the general behavior of pesticides applied as granule formulations in a paddy field. This can be quantified by considering the main pro-

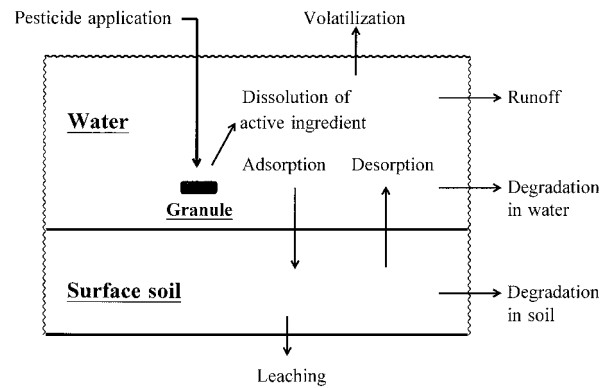


Figure 1. Behavior of pesticides applied as a granule formulation in paddy fields.

cesses: dissolution of pesticide from the granule into water, adsorption and desorption, run-off, leaching, volatilization and degradation. In this model, the process of pesticide uptake by plants was not considered.

The conceptual model for the behavior of pesticides in paddy fields in the form of a compartment system is described by Fig. 2. The following assumptions were made in the development of PADDY: (1) This system consists of a surface and a sub-surface layer. (2) The surface layer is composed of paddy field water (surface water) and surface soil phase; the latter is composed of pore water and soil solid compartments under flooded conditions. (3) The thickness of the surface soil phase is 5 mm (active soil layer), and the pore water is included in the paddy field water. (4) The sub-surface layer is composed of pore water and soil solid compartments, and the thickness of each layer is 5 mm. (5) The driving force of mass transfer between compartments arises from the gradient of the pesticide concentration in each compartment. (6) When pesticides enter each compartment, pesticides are instantaneously mixed with the entire contents and distributed uniformly (i.e. completely mixed condition). (7) The volumetric

flow rate into and out of paddy field is constant (i.e., inflow rate = outflow rate + penetration rate + evaporation rate = constant), and the volume of paddy-field water is constant.

2.3 Description of the inter-phase mass transfer processes

2.3.1 Granule formulation–water

Dissolution of pesticides from granule formulations into water is expressed by the diffusion-layer theory of the Nernst-Brunner model.²

$$\frac{dC_w}{dt} = \frac{DS}{Vh} (C_{ws} - C_w) \quad (1)$$

D and C_{ws} show constant values at a certain temperature. V and h are also constants if dissolution is performed under controlled conditions. Strictly, S is not constant because it decreases as the pesticide

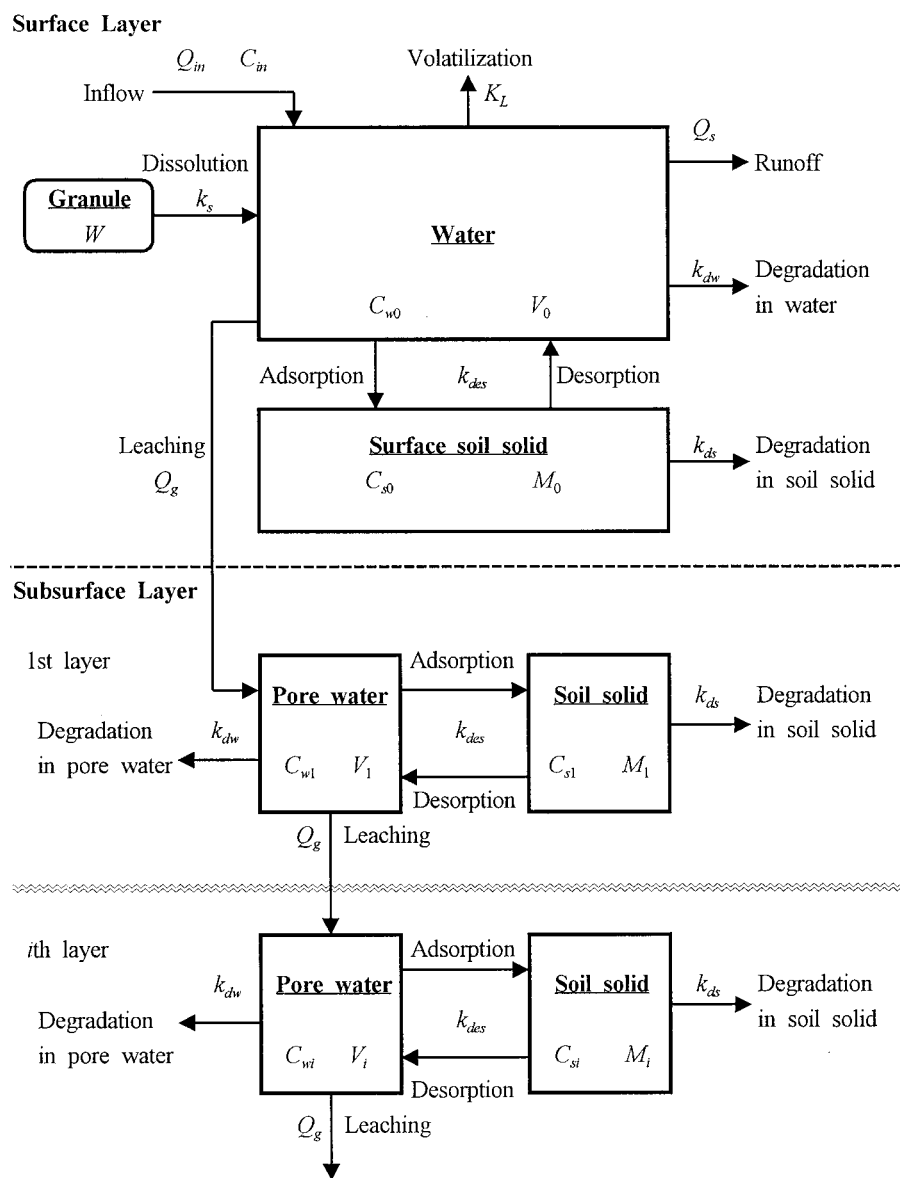


Figure 2. The compartment system in the paddy field. See Section 2 for notation.

is dissolved. However, because it is difficult to measure S , it is handled as if it were a constant. Therefore, eqn (1) can be written as,

$$\frac{dC_w}{dt} = k_s(C_{ws} - C_w) \quad (2)$$

2.3.2 Water-soil

The sorption rate equation is expressed based on a one-site system,³ using the Freundlich sorption isotherm equation.

$$\frac{dC_s}{dt} = k_{des}(K_f C_w^{1/n} - C_s) \quad (3)$$

2.3.3 Water-air

The interface transfer from water to air is expressed by the two-layer (film) model of a gas-liquid inter-

face of Lewis and Whitman.⁴

$$V \frac{dC_w}{dt} = -K_L A C_w \quad (4)$$

2.4 Degradation processes

In this model, degradation processes in water and soil are expressed as a first-order reaction. Degradation in water and soil is expressed by,

$$\frac{dC_w}{dt} = -k_{dw} C_w \quad (5)$$

$$\frac{dC_s}{dt} = -k_{ds} C_s \quad (6)$$

The degradation rate constants are the sum of first-order-decay rates due to both abiotic (hydrolysis and photolysis) and biotic processes.

2.5 Transport processes

Pesticide inflow, run-off, and leaching are given by,

$$V \frac{dC_w}{dt} = Q_{in} C_{in} - Q_s C_w - Q_g C_w \quad (7)$$

2.6 Mass balance equations in the paddy field

When all flows (Q_{in} , Q_s , and Q_g) and V are constant ($dV/dt = 0$) and pesticide concentration in inflow is zero ($C_{in} = 0$), the mass balance equations for the surface layer are as follows:

for the granule formulation

$$\frac{dW}{dt} = -V_0 k_s (C_{ws} - C_{w0}) \quad (8)$$

for the water compartment

$$\begin{aligned} V_0 \frac{dC_{w0}}{dt} = & V_0 k_s (C_{ws} - C_{w0}) - Q_s C_{w0} - Q_g C_{w0} \\ & - M_0 k_{des} (K_f C_{w0}^{1/n} - C_{s0}) \\ & - K_L A C_{w0} - V_0 k_{dw} C_{w0} \end{aligned} \quad (9)$$

for the soil solid compartment

$$M_0 \frac{dC_{s0}}{dt} = M_0 k_{des} (K_f C_{w0}^{1/n} - C_{s0}) - M_0 k_{ds} C_{s0} \quad (10)$$

and the equations for the subsurface layers are:

for the pore water compartment of the i th layer

$$\begin{aligned} V_i \frac{dC_{wi}}{dt} = & Q_g C_{wi-1} - Q_g C_{wi} \\ & - M_i k_{des} (K_f C_{wi}^{1/n} - C_{si}) - V_i k_{dw} C_{wi} \end{aligned} \quad (11)$$

for the soil solid compartment of the i th layer

$$M_i \frac{dC_{si}}{dt} = M_i k_{des} (K_f C_{wi}^{1/n} - C_{si}) - M_i k_{ds} C_{si} \quad (12)$$

When dissolution of the pesticide from the granule is completed ($W = 0$), the dissolution rate (k_s) is set to zero in eq (8) and (9).

These ordinary differential equations can be solved by use of the Runge–Kutta–Gill method, and numerical solutions provide pesticide concentrations in water and soil solid as a function of time t . A computer program, PADDY, was developed utilizing BASIC language.

2.7 Pesticides

To evaluate this model, two herbicides: molinate (*S*-ethyl azepane-1-carbothioate) and simetryn (N^2 , N^4 -diethyl-6-methylthio-1,3,5-triazine-2,4-diamine), was applied. These herbicides have been widely used for the control of broad-leaved weeds in paddy fields in Japan. The granule formulation used for all the experiments was a molinate 80, simetryn 15 g kg⁻¹

granule (Mamet-SM), which is applied under flooded conditions of about 5 cm depth of water.

2.8 Methods for measurement and estimation of model input parameters

2.8.1 Dissolution rate from granule formulation (k_s)

Measurement of dissolution rate was performed using the batch method. Distilled water (1500 ml), corresponding to about 5 cm depth of water, was put into a cylindrical glass jar (150 mm 200 mm ID), and granule formulation (0.1 g) to represent the recommended normal dose was added to the jar; the jar was covered with a glass plate to prevent evaporation of water, and set in a water bath kept at 20 or 30°C in dark conditions. At various intervals of time (0.5, 1, 3, 6, 24, and 48 h after application), aliquots of the water sample (5–10 ml) were collected with a pipette from the centre of the water level at 2.5 cm depth, and pesticide concentrations were determined. These were used to calculate the dissolution rate (k_s) as given in Section 3.2.1.

2.8.2 Desorption rate (k_{des})

Desorption rate was measured by use of a soil column. Glass columns (250 × 40 mm ID), fitted with a stop cock at the bottom to allow dripping of water and tracked at the bottom with glass wool and sea sand, were fitted with water-saturated soil collected on the paddy field where the field experiment was carried out. The depth of the soil column varied from 5 to 50 mm. The columns were wrapped with aluminium foil and stored vertically at room temperature. Aqueous pesticide solution (about 5 mg litre⁻¹; 62 ml), corresponding to about 5 cm depth of water, was applied at the top of each soil column, and penetrated slowly through the soil column. The leachate was analysed for pesticide residues, and the amounts of pesticide sorbed in soil were estimated. Distilled water (62 ml) without test pesticide was then added to the column. After 6 h, surface water was collected slowly by pipette so as not to suck up the soil solids. Amounts of pesticide desorbed from soil were analysed, and pesticide concentrations in soil were estimated. These operations were repeated at various intervals (24, 51, and 75 h after treatment), and a concentration–time profile of pesticides in the soil was obtained. Desorption rate (k_{des}) was calculated using linear regression procedures on the plot of the natural log of pesticide concentration in soil as a function of time.

2.8.3 Overall mass transfer coefficient (K_L)

Liss and Slater,⁵ and Mackay and Leinonen⁶ have published an estimation method of the overall mass transfer coefficient based on a two-layer model of Lewis and Whitman. K_L is calculated by eqns (13)–(15).

$$K_L = \left(\frac{1}{k_l} + \frac{1}{Hk_g} \right)^{-1} \quad (13)$$

$$k_l = 4.752 \times \sqrt{\frac{44}{MW}} \quad (14)$$

$$k_g = 720 \times \sqrt{\frac{18}{MW}} \quad (15)$$

H is estimated by the Dilling equation,⁷

$$H = \frac{16.04 \times MW \times VP}{C_{ws} \times T} \quad (16)$$

2.8.4 Soil sorption coefficient (K_f , $1/n$)

K_f and $1/n$ were measured using the OECD test guideline.⁸ The soil used in this experiment was collected on the paddy field where the field experiment was carried out.

When a Freundlich isotherm equation is not obtained, K_d (i.e. the ratio of the pesticide concentration on the soil solid to the concentration in solution at equilibrium) can be used. In this case, $1/n$ value is equal to 1. When experimental values are unavailable, K_{oc} is calculated by Kenaga and Goring's equation,⁹

$$\log K_{oc} = -0.55 \times \log C_{ws} + 3.64 \quad (17)$$

and the K_d value can be calculated from oc .

$$K_d = K_{oc} \times \frac{oc}{100} \quad (18)$$

2.8.5 Degradation rate in water (k_{dw}) and soil (k_{ds})

Measurement of degradation rate in water was performed by the batch method. Water (500 ml), collected from outdoor paddy fields without filtration and sterilization, was taken into a 1000-ml glass beaker, corresponding to about 5 cm depth of water. Standard pesticide solutions in acetone were added to the water to produce a final pesticide concentration of 1 mg litre⁻¹. The glass beaker was covered with a glass culture dish to prevent evaporation of water, and incubated on outdoor paddy fields. At various intervals of time (0, 1, 3, 7, 14, 28, 45 and 60 days after treatment), aliquots of the sample (5 ml) were collected from the beaker with a pipette for analysis, and pesticide residues were determined. Degradation rate in water (k_{dw}) was calculated using linear regression procedures on the plot of the

natural log of pesticide concentration in water as a function of time. If a reference value of $DT_{50water}$, comprising hydrolysis, photolysis, and biodegradation is available, k_{dw} can be calculated by,

$$k_{dw} = \frac{0.693}{DT_{50water}} \quad (19)$$

Degradation rate in soil (k_{ds}) was estimated from DT_{50soil} by the following equation,

$$k_{ds} = \frac{0.693}{DT_{50soil}} \quad (20)$$

DT_{50soil} values of two herbicides were assumed from reference data of laboratory experiments on degradation in soil under a flooded condition.^{10,11}

2.9 Field experiment for model evaluation

To validate the model, a field experiment was carried out on a paddy field in Tokyo, Japan. The layout of the paddy field for the experiment, and the soil conditions are shown in Fig. 3 and Table 1, respectively.

The two herbicides were applied as the granule formulation at 10 days after transplanting (24 June, 1991). The granule was applied at the rate of 3 kg 1000 m⁻² (molinate 2400 g ha⁻¹, simetryn 450 g ha⁻¹), representing the recommended normal dose, by hand into the paddy field under flooded conditions, and the water depth was kept about 3 cm.

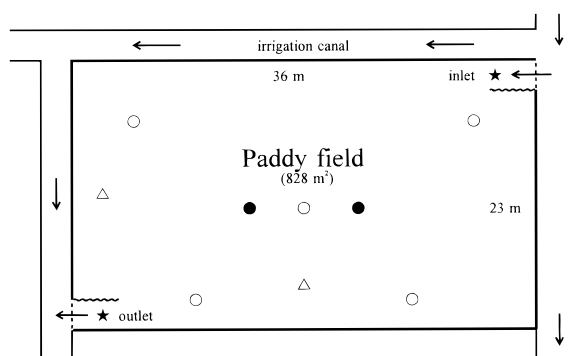
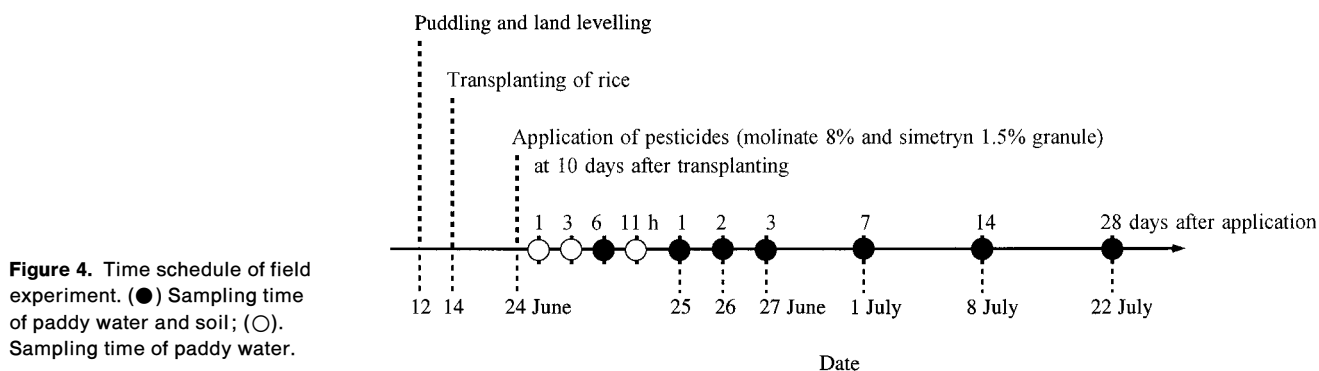


Figure 3. Layout of paddy field for experiment. (○) sampling site of paddy water and measurement site of water depth; (●) sampling site of soil; (★) measurement site of flow rate; (Δ) measurement site of fall in water depth and evaporation rate of water; Arrows (→) indicate water movement.

Table 1 Soil characteristics of the experimental paddy field

Sampling site	Tokyo
Soil texture ^a	Light clay
Clay content (%)	33.8
Silt content (%)	34.2
Sand content (%)	32.0
Organic carbon content in soil (%)	4.62
pH (H ₂ O, 1:2.5)	6.0
Cation exchange capacity (me 100 g ⁻¹)	23.4
Bulk density of dry soil (g cm ⁻³)	0.60 (0–2 cm), 0.71 (2–4 cm)
Porosity	0.56 (0–2 cm), 0.46 (2–4 cm)

^a According to the International Society of Soil Science system (ISSS).



During the experimental period, inflow and outflow rates of water, fall in water depth and evaporation rate of water were measured at each sampling time. Polyvinyl chloride pipes (300 × 200 mm ID) were driven into the soil to about 15 cm in depth at two sites in the field (see Fig. 3) and the fall in water depth in a day was determined by measuring the water level difference inside the pipes. The evaporation rate from water was determined by measuring the reduction in water level inside a 500-ml plastic cylinder set in the field. The daily penetration rate was calculated by subtracting the daily evaporation rate from fall in water depth in a day.

Water and soil samples were taken at various times (see Fig. 4). Water samples were collected by a 200-ml glass beaker at five sampling sites in the field (see Fig. 3), and mixed for analysis. Soil samples were collected by a soil sampling tube (50 × 50 mm ID) at two sampling sites (see Fig. 3), and separated into two layers (0–20 mm and 20–40 mm depth), and analyzed individually.

Water samples were percolated through a solid-phase extraction cartridge (Waters SEP-PAK tC18), and the cartridge was eluted with dichloromethane, the eluent evaporated to dryness, and dissolved in hexane. Soil samples were extracted twice by shaking with aqueous acetone, partitioning into dichloromethane and cleaning up with a florisil cartridge (Waters SEP-PAK FLORISIL). Pesticides residues were determined using a gas chromatograph with

nitrogen-phosphorus detector. The limits of determination for the two herbicides in water and soil were $0.1 \mu\text{g litre}^{-1}$ and $10 \mu\text{g kg}^{-1}$, respectively. Duplicate analysis of pesticides was performed.

3 RESULTS

3.1 Environmental conditions

Environmental conditions of the model paddy field are shown in Table 2. These values were set from experimental data. The average evaporation and penetration rates of water during the experimental period were 0.1 and 0.95 cm day^{-1} , respectively.

3.2 Pesticide parameters

Table 3 shows physiochemical properties, equilibrium constants, and rate constants for molinate and symetryn, which were measured or estimated values. It was assumed that the adsorption coefficient, desorption rate, and degradation rate in water and soil in sub-surface layers were equal to those in the surface layer.

3.2.1 Dissolution rate constant

Figure 5 shows the concentration–time profiles of the dissolution of molinate from the granule at 20 and 30°C. Dissolution rate was influenced by temperature, and dissolution at 30°C was faster than at 20°C. As shown in Fig. 5, the dissolution rate was greatest at the beginning of dissolution and

Table 2 Conditions of the model paddy field

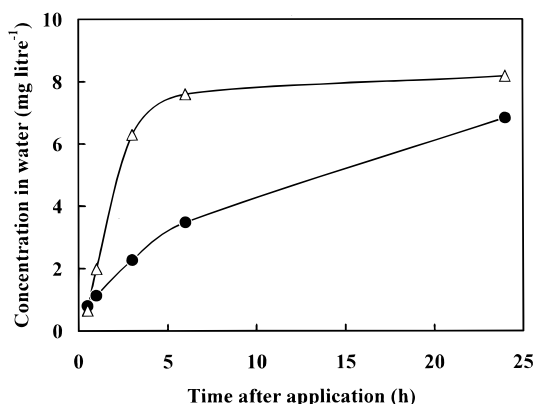
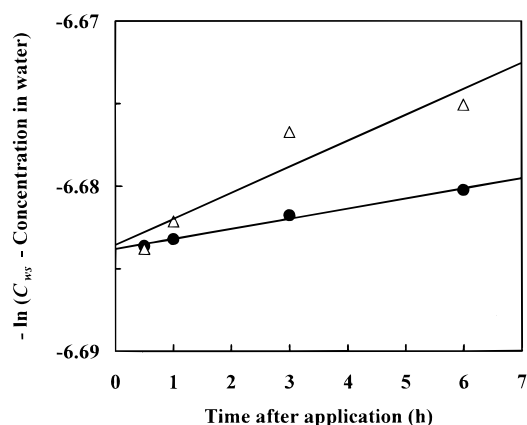
Parameter	Value
Area (A ; m^2)	1000
Depth of field water (m)	0.032 ^a
Depth of surface soil (m)	0.005
Thickness of each sub-surface layer (m)	0.005
Volume of water	
Field water (V_0 ; m^3)	32 ^a
Pore water in each sub-surface layer (0–2 cm; m^3)	2.8
Pore water in each sub-surface layer (2–4 cm; m^3)	2.3
Weight of soil	
Surface soil (M_0 ; kg)	3000
Sub-surface soil in each layer (0.5–2 cm; kg)	3000
Sub-surface soil in each layer (2–4 cm; kg)	3550
Outflow rate of water (Q_s ; $\text{m}^3 \text{day}^{-1}$)	7.7 ^a
Penetration rate of water (Q_g ; $\text{m}^3 \text{day}^{-1}$)	9.5 ^a

^a Average value during the experimental period.

Parameter	Molinate	Simetryn
Physicochemical properties		
Relative molecular mass (MW)	187.3	213.3
Water solubility (C_{ws} ; mg litre ⁻¹)	800 (20°C)	450 (20°C)
Vapour pressure (VP; mm Hg)	5.7×10^{-3} (25°C)	7.1×10^{-7} (20°C)
Equilibrium constants		
Henry's constant (H)	7.2×10^{-3} ^a	1.8×10^{-8} ^a
Adsorption coefficient (K_f ; litre kg ⁻¹)	7.9 ^b	13.1 ^b
[Freundlich exponent (1/ n)]	0.96 ^b	0.75 ^b
Rate constants		
Dissolution (k_s ; day ⁻¹)	3.1×10^{-2} ^b	9.6×10^{-3} ^b
Desorption (k_{des} ; day ⁻¹)	2.9×10^{-1} ^b	1.5×10^{-1} ^b
Volatilization (K_L ; m day ⁻¹)	1.6×10^{-2} ^c	3.8×10^{-6} ^c
Degradation in water (k_{dw} ; day ⁻¹)	1.9×10^{-2} ^b	4.7×10^{-3} ^b
Degradation in soil (k_{ds} ; day ⁻¹)	1.7×10^{-2} ^d	1.4×10^{-2} ^d

^a Calculated by eqn (16).^b Measured value.^c Calculated by eqns (13)–(15).^d Estimated from References 10 and 11.**Table 3.** Model input parameters of molinate and simetryn

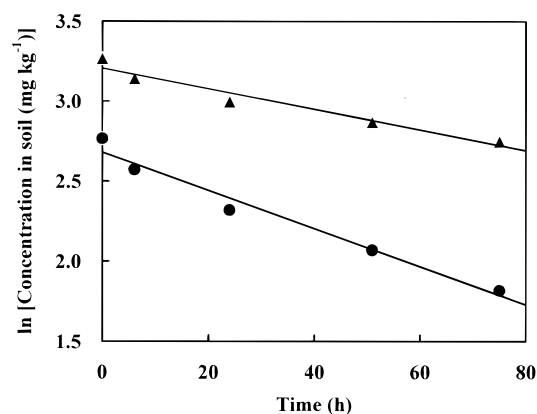
decreased gradually with time. Therefore, the dissolution rate cannot be expressed as a first-order reaction. However, as shown in Fig. 6, the dissolution rate can be regarded as a first-order reaction at the beginning of dissolution (within 6 h after

**Figure 5.** The effect of temperature on dissolution of molinate from the granule formulation: dissolution curve at (●) 20°C; (△) 30°C.**Figure 6.** Determination of dissolution rate of molinate from the granule formulation. C_{ws} is water solubility of pesticide (mg litre⁻¹). Dissolution curve at (●) 20°C; (△) 30°C.

application), and it can be calculated using linear regression procedures on the plot of $[-\ln(C_{ws} - \text{concentration in water})]$ as a function of time.

3.2.2 Desorption rate constant

Figure 7 shows the measured concentration–time profiles of the desorption of the two herbicides in soil, which followed a first-order reaction. Table 4 shows the total amounts of the pesticide desorbed

**Figure 7.** Concentration–time profiles of (●) molinate and (△) simetryn in soil due to desorption. Soil thickness is 5 mm.**Table 4.** Total amounts of pesticides desorbed from the soil over 75 h

Depth of soil column (cm)	Molinate (μg)	Simetryn (μg)
0.5	40.3	43.8
1.0	39.9	36.5
2.0	38.6	35.8
3.0	38.9	41.7
5.0	40.1	44.5

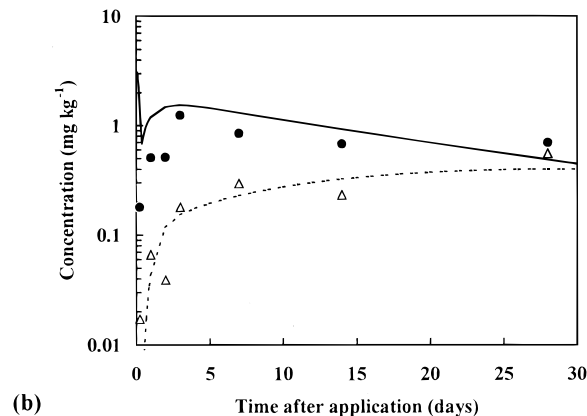
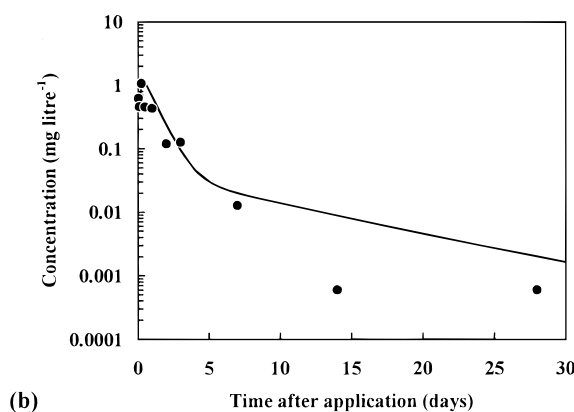
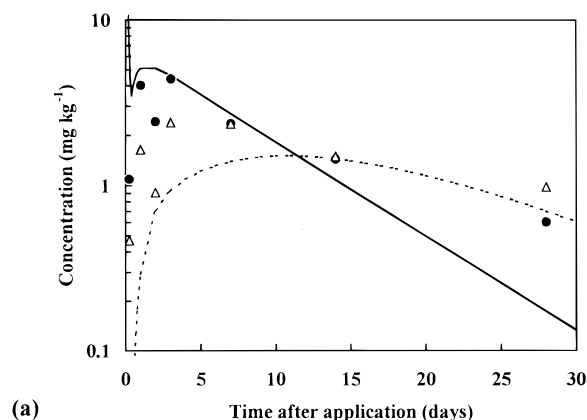
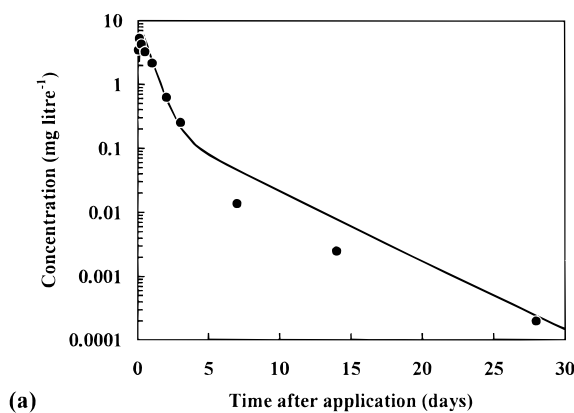


Figure 8. Comparison between (—) calculated and (●) measured concentration in paddy water. (a) molinate; (b) simetryn.

Figure 9. Comparison between calculated and measured concentration in soil. (a) molinate; (b) simetryn. (—) calculated and (●) measured concentrations in 0–2 cm depth (mg kg^{-1}). (---) calculated and (Δ) measured concentrations in 2–4 cm depth (mg kg^{-1}).

from the soil over 75 h when the soil thickness was changed from 5 to 50 mm. Soil thickness had no influence on the total amounts of desorbed pesticides.

3.3 Comparison between model prediction and field data

Figures 8 and 9 show the measured and predicted concentration profiles in water and soil, respectively. The measured concentration of pesticides in water increased immediately after application, and reached maximum concentrations at 3 or 6 h after application (molinate: $5.27 \text{ mg litre}^{-1}$ at 3 h, simetryn: 1.06 mg litre at 6 h), thereafter decreasing rapidly with the lapse of time. At one week after application, the dissipation had become slow. In the 0–2-cm soil layer, the concentration of pesticide increased immediately after application and, three days later,

reached maximum (molinate: 4.41 mg kg^{-1} , simetryn: 1.24 mg kg^{-1}), thereafter decreasing gradually. In the 2–4 cm layer, the concentration of molinate reached the maximum (2.40 mg kg^{-1}) at three days after application and then decreased gradually with the lapse of time. The concentration of simetryn increased gradually and reached the same level as the concentration in 0–2 cm 30 days after application.

The predicted concentrations in each compartment up to 4 cm depth were calculated by PADDY using the input parameters obtained by the above-mentioned method (Tables 2 and 3). The average concentrations in the 0–2 and 2–4 cm soil layers were calculated from the sum of concentrations in pore water and soil solid. Until dissolution of the pesticide

Table 5. Contribution to disappearance processes in water and soil for 30 days calculated by PADDY

Disappearance process	Molinate (% of initially applied)	Simetryn (% of initially applied)
Volatilization to air	37.0	0.0
Run-off	40.6	61.9
Leaching below 40 mm depth in soil	12.2	1.8
Degradation in surface water	1.4	0.5
Degradation in soil layer (0–40 mm depth) ^a	6.8	13.1

^a Composed of pore water and soil solid.

from the granule was complete, the pesticide amount remaining in the granule was added to the 0–2 cm soil layer figures. PADDY followed the trend of measured concentration changes well.

Table 5 shows the contribution of the various processes to the disappearance of the two herbicides over 30 days, calculated by PADDY. The major disappearance processes for molinate were run-off (40.6%), volatilization (37.0%), and leaching below 40 mm depth in soil (12.2%), and that of simetryn was run-off (61.9%).

4 DISCUSSION AND CONCLUSION

PADDY was constructed under the assumptions that the pore water of the surface soil phase was included in the paddy field water and that the thickness of the surface soil phase was 5 mm. Desorption rate measurements showed that there was no difference in the total amounts of desorbed pesticides when the soil thickness was changed from 5 to 50 mm. It was suggested that the thickness of the active soil layer, where the adsorption and desorption of pesticides occurs effectively between paddy field water and soil solid, is about 5 mm or less.

As shown in Figs 8 and 9, the concentrations predicted by PADDY were in reasonably good agreement with the field measurement data. The predicted concentrations were generally within a factor of three of the measured concentrations. However, the predicted concentrations of molinate in the 2–4 cm soil layer were underestimated within three days after application. It was thought that the soil samples were contaminated at the soil sampling.

As shown in Table 5, the run-off amount of the two herbicides was so great, because the outflow rate of water was fast in this field experiment, compared with a normal condition. For this granule, the required water-holding period is three to four days. However, water was not held in the experimental field, and water flowed continuously on the field. Daily discharge rate of paddy field water, R_d (% day⁻¹), that is, the ratio of Q_s to V , was 55.4% in this experiment. Normally, R_d is about 10%. When R_d was set to 10% [$Q_s = 3.2$ (m³ day⁻¹), and other parameters were the same in Tables 2 and 3], the run-off contributions of molinate and simetryn by PADDY were 10.8% and 23.0%, respectively.

For the two herbicides, degradation in water was not significant, because the degradation rates in water were not large. The half-lives in water of molinate and simetryn were 36 days and 136 days, respectively. Soderquist *et al.*¹² reported that volatil-

ization was the major dissipation process for molinate in the paddy field. Our estimation by PADDY was in agreement with this report.

Results of evaluation of the model suggest that PADDY is a useful tool for predicting pesticide concentrations and evaluating the key processes of the fate in paddy fields. Although PADDY is not a model for detailed site-specific evaluation, concentration profiles calculated by PADDY may be utilized to estimate average concentrations occurring in aquatic ecosystems under a standard scenario.

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